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Electronic and Total Energy Properties of Ternary and Quaternary Semiconductor Compounds, Alloys and Superlattices

Theoretical Study of Cu/Graphite Bonding

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(NASA-CR-190691) ELECTRONIC AND TOTAL ENERGY PROPERTIES OF TERNARY AND QUATERNARY SEMICONDUCTOR COMPOUNDS, ALLOYS, AND SUPERLATTICES: THEORETICAL STUDY OF Cu/GRAPHITE BONDING Technical Report, Jan. 1991 - Jan. 1992 (Case Western Reserve Univ.) 22 p

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1 Introduction

HISTORY: The subject of this grant, which was originally concerned with the study of semiconductor alloys and heterostrucutures of use for photovoltaic applications was changed in the last year (1991) to a study of metal/graphite bonding in view of the interest in this subject in the Materials Branch (Dr. Stephen Pepper) at NASA Lewis Research Center. Progress reports on the previous year's activities were given in the renewal proposals.

MOTIVATION: The study was focused on Cu/graphite bonding in view of its practical importance in graphite fiber enforcement of Cu for applications where high thermal conductivity is important. The technological problem is that the interfacial bonding between Cu and graphite fibers is extremely weak.

PREVIOUS WORK: Wetting studies of the graphite basal plane at NASA LeRC by De Vincent et al. [1] by Cu and Cu with various alloy additions confirmed this and also indicated that small amounts of Ti and Cr could lead to better bonding.

GOALS: The goals of this proposal were:

1. To provide a fundamental science basis for why the bonding of Cu to graphtie is weak.
2. To critically evaluate the previous analysis of the wetting studies, in particular with regards to the values used for surface enrgies of Cu and graphite.
3. To make recommendations for future experiments or other studies which could advance the understanding and solution of this technological problem.

2 Approach

First-principles electronic structure calculations were used to study the problem. These are based on density fucntional theory in the local density ap-

proximation [2] and the use of the linear muffin-tin orbital band-structure method [3].

Calculations were performed for graphite monolayers, single crystal graphite with the hexagonal AB stacking, bulk Cu, Cu {111} surface and Cu/graphite superlattices. The study is limited to the basal plane of graphite because this is the graphite plane exposed to Cu in the graphite fibers.

A critical study was made of the available literature on Cu and graphite surface energies and combined with the measured contact angles to evaluate the experimental adhesion energy.

3 Technical details and results

For this initial study, we attempted to use the linear muffin-tin orbital method (LMTO) in the so-called atomic sphere approximation (ASA). This is the simplest version of the method which has the advantage of being computationally cost effective and easy to use. The disadvantage is that the approximations made limit the accuracy for certain types of problems. Unfortunately, severe limitations due to the method were discovered for the present problem. Although qualitative conclusions about the electronic structure and insights in the origin of the weak bonding could be obtained, it was impossible to obtain quantitative results for adhesion or surface energies for the system under study using this computational approach. This problem could be solved by using the so-called full-potential LMTO method. The time and resources available for this grant, however, did not allow us to carry out these more demanding calculations. Instead, we decided to provide some semi-quantitative results using literature data on surface energies and the measured contact angles of the wetting studies. We also discuss some of the literature available on metal/graphite interaction. Below, we first consider the results of the ASA-LMTO calculations and next, the results of our literature studies.

3.1 Computational Results

3.1.1 Graphite

We started out with a study of bulk and monolayer graphite. The problem with the ASA-approach is that it is only applicable to systems of reasonably

close-packed spheres. Graphite is a very open structure as is evident from the weak coupling between the layers and the rather open honeycomb lattice in the 2D-layers. The system can nevertheless be described in terms of close-packed sphere assemblies by introducing a large number of empty spheres. By placing empty spheres in the hexagon centers of a graphite layer, one produces a closed packed layer of spheres. Close-packed stacking of similar layers, some completely consisting of empty spheres and some with carbon and empty spheres allows us to build up the graphite structure. Bulk graphite with the AB stacking is obtained by inserting two layers of empty spheres. The graphite layers become almost completely decoupled when three layers of empty spheres are inserted. This allows us to study both a monolayer and the actual crystal structure of graphite. We can slighlty change the size of the empty spheres inserted between the graphite layers and thus modify c/a of the structure.

The band structures obtained at the experimental lattice constants for monolayer and bulk graphite are shown in Figs. 1-2. These results are in excellent agreement with previous calculations in the literature [4, 5, 6] including the weak splittings of the bands in induced by the coupling of the layers in the bulk graphite crystal structure.

Fig. 3 shows the monolayer density of states (DOS), which is very similar to that of bulk graphite. Note the position of the Fermi level at the DOS minimum in between the π-bonding and anti-bonding peaks, related to the critical points at M. The high peak in the range -10 to -8 eV corresponds to a region of overlap between the σ and π bands.

The total energy calculations revealed a problem with the ASA. It was impossible to obtain a meanignful c/a ratio and even when c/a was fixed to the experimental value the theoretical equilibrium lattice constant a was 10 % larger than the experimental value. Correspondingly, the cohesive energy was 36 % too large. Typically for semiconductors or close-packed metals, the ASA yields the lattice cosntant to within a few % and the cohesive enrgies are $\sim$10 % overestimated. We atribute this failure to the inadequate description of the charge density tails inside the empty interstitial region. The ASA makes a spherical approximation to the latter inside each atomic sphere. Since these charge densities decay to almost zero over the length scale of a sphere, there must be strong dipoles which have not been taken into account. This misrepresentation of the intersitital charge densitiy in turn affects the bonding in the layers. Similar problems are known to occur

for surfaces (see next section on Cu). A possible solution to this problem would be to incorporate the dipole moments of the charge densities inside the spheres. The program modifications required to do this could not be acomplished within the limited timeframe of this grant. A better solution, would be to use the full-potential version of the LMTO method, in which charge density and potential are allowed to be completely general. Programs to do this are already available.

We decided nevertheless to continue the ASA investigation with the more limited goal of providing insights in the electronic structure. The latter appeared to be adequately described by the approach.

3.1.2 Copper

In preparation to the calculation of Cu/graphite interfaces, we needed to calculate Cu and the Cu surface with a similar stacking of interstitial empty spheres as used for the graphite calcualtion. This facilitates the description of the interface system since this allows the same assembly of close-packed and almost equal size spheres to be used for the various systems.

The test for bulk Cu total energy properties (equilibrium lattice constant, bulk modulus, cohesive enrgy) yielded excellent agreement with a standard calculation in which no empty spheres are used.

Next, we proceeded to the surface calculations. A supercell of 6 layers of Cu separated by empty sphere layers was used. The resulting surface and bulk-like (center of Cu-slab) densities of states (DOS) are shown in Fig. 4. They show the well known narrowing of the surface LDOS compared to the bulk DOS which is due to the reduced coordination. Again, however, the surface energy γ^s defined as the total energy difference between the surface slab and an equivalent number of bulk atoms, is very much overestimated. These results are similar to what is obtained using a more conventional sphere packing.

From the work of Skriver and Rosengaard [7], we know that this problem is essentially related to the neglect of the intra-sphere dipole moment perpendicular to the surface. As for graphite, the results are satisfactory for a qualtitative study of the electronic structure, but not for a quantitative evaluation of surface energetics.

3.2 Cu/graphite interface

In order to study the Cu/graphite interface, we employ a supercell consisting of 4 layers of Cu in a hcp stacking and 1 layer of graphite. This stacking is repeated periodically and describes the essential local bonding of the

Cu:fcc {111}|| C:graphite {0001}

configuration. (The reason for choosing a hcp Cu stacking is that we need to have a reflection symmetry in the graphite layer in order to have two equivalent interfaces and want to reduce the number of atoms per cell. With just 4 Cu layers, the easiest solution was to stack them in hcp order. This has no effect on our conclusions.)

One layer of empty spheres is placed between Cu and graphite, leading to an ideal structure with a Cu C distance of 2.08 Å as a starting point for our investigations. This distance is ~0.1 Å smaller than a typical M-C distance in transition metal carbides. It is thus expected to allow considerable interaction between Cu and graphite. The C C distance in the plane is 1.47 Å, slightly larger than that in graphite (1.42 Å). Nevertheless, the band structure of this graphite monolayer is still essentially that of graphite, characterized by strong σ and π-bonding.

The layer projected densities of states (DOS) obtained in this model are shown in Fig. 5. The Cu and graphite DOS are essentially unperturbed from the corresponding bulk DOS. Furthermore, the Cu $3d$ band lies well separated from the majority of C states, falling in the low DOS region near the Fermi energy. This is clearly indicative of a weak interaction between the two. Upon closer inspection, one may notice an upward shift by ~0.7 eV of the position of the Cu $3d$ band peak with respect to the Fermi level on the interface layer. The Fermi level on the graphite monolayer can be seen to lie ~ 1.6 eV higher than in the isolated monolayer, where it occurs at the minimum in the DOS indicated by the arrow in Fig. 5. This is clearly indicative of a charge transfer from Cu to the graphite. Because of the empty spheres, it is not straightforward to assign the charge transfer quantitavely on the basis of the calculated sphere charges. From the area under the LDOS curve between the Fermi level position in bulk graphite and at the Cu/graphite interface, we estimate that ~0.1 electron/C-atom have beeen transferred to graphite. Notice, however, that in our model there is a Cu layer on each side of the graphite monolayer. For a monolayer absorbed

on Cu, we would thus expect a smaller charge transfer. We note here that for bulk graphite in contact with bulk metal, the bulk Fermi levels must, of course, be aligned. The local shifts of the Fermi level near the interface seen here, must thus be interpreted as an opposite shift of the bands (and thus the local potential) with respect to the fixed Fermi level.

We note that there exists experimental evidence for metal to graphite charge transfer in other metal systems. (See next section.) Unfortunately, we could not determine quantitatively how this affects the total energy of bonding (i.e. the adhesion energy).

In the calculations described above the Cu was placed directly above the C atoms of the graphite. An alternative position would be to place it over the holes in the honeycomb structure. Furthermore, the distance between C and Cu should be adjusted to minimize the energy. Because of the inaccuracies encountered in the ASA calcualtion of total energies for graphite and Cu surfaces, we did not attempt to do so. The interatomic distances of our idealized sphere packing probably place us in the repulsive range of the interaction. Expanding these distances, however, we change the overlap between the spheres too much to allow any meaningful comparison between their total energies. We did a calculation for another Cu position, and found qualitatively similar conclusions about weak bonding and charge transfer. The details of the DOS near the Fermi level were found to depend on the details of the structure. Since we could not optimize the structure, we cannot attach too much importance to a detailed analysis of these features in the electronic structure.

3.2.1 Discussion and Conclusions

The electronic structure results show that the bonding between Cu and graphite is weak. Basically, no chemical bonds are formed as is indicated by the LDOS figures. The reason for this is that the graphite monolayer is almost like a closed shell system. The strong π-bonding related to the close interactomic distances between carbon atoms in the layer leaves no electrons free in "dangling bonds" to couple to a metal. The Cu d-band itself is practically filled. Thus only the Cu 4s is available for making bonds. The interaction results basically from a weak overlap between the charge density tails. Basically the repulsive core-core interactions dominate and only a very weak Van-der-Waals-type of bonding results. There is some weak coupling

to the π-electron system which results in some charge transfer. This may have some effect on the bonding strength.

3.3 Literature Study

3.3.1 Graphite surface energy

Since graphite is a layered material with weak interlayer bonding, it is obvious that the surface energy of the basal plane must be very weak. Basically, the surface energy γ^s in this case is half the interlayer coupling in bulk graphite, properly normalized per unit area. Several studies were dedicated to calculating the interlayer coupling in graphite.

The values are summarized in Table 1.

Table 1: Surface energy of graphite {0001}

Ref.	γ^s (mJ/m^2)
Brennan[8]	70
DiVincenzo et al. [9]	330
Jansen and Freeman [6]	250
Good et al. [11]	120

- Brennan [8] using lattice summations of semi-classical interatomic forces based on quantum chemical calculations, obtained a value ofr γ^s of 70 mJ/m^2.
- The work of DiVincenzo et al. [9] is based on density functional theory. It estimates the interlayer charge density by superposition of the charge density tails of self-consistently calculated monolayers and treats the kinetic energy by means of gradient expansions instead of using a Kohn-Sham calculation. These authors, in addition showed that the bonding between the layers is rather structure insensitive since similar values were obtained using a 2D averaged model charge density. They give a very interesting account of the relations between the classical Van der Waals interaction to the density fucntional theory. The value obtained for γ^s is 330 mJ/m^2.

- The most accuate calculations of bulk graphite were performed by Jansen and Freeman [6] using LAPW and by Yin and Cohen [10] using the norm-conserving pseudopotential plane wave method. Jansen and Freeman provide an estimated value for the energy difference between the monolayer end the bulk crystal, from which we extract a value for the surface energy $\gamma^s = 250$ mJ/m^2. This number, however, is based on a comparsion between calculations performed with slightly different LAPW codes. (The somewhat older film-LAPW version was used for the monolayer calculation.)

- An experimental value for the surface energy was obtained by Good et al. [11]. These results are based on measuring the heat of immersion in various organic fluids whose surface energies are known. The value obtained was 120 mJ/m^2.

DISCUSSION: The DFT values seem to be larger than the experimental value. Density functional theory is known to overestimate cohesive energies and thus is likely to overestimate the surface energy by $\sim$10 %. There are probably rather large uncertainties also on the experimental value and the older semi-empirical calculation of Brennan. We can probably safely say that $\gamma^s \leq 0.2 \pm 0.1$ J/m^2.

3.3.2 Copper

Several calculations exist of the surface energy of Copper. The values are summarized in Table 2.

Table 2: Surface energy of Cu {111} at $T = 0$

Ref.	γ^s (mJ/m^2)
Appelbaum & Hamann [12]	2016
Smith & Banerjea [13]	1830
Skriver [14]	1997
Miedema [15]	1825
Wawra [16]	2000

- Applebaum and Hamann [12] used self-consistent slab calculations with an atomic orbital basis.

- Smith and Banerjea[13] used the so-called equivalent crystal theory.

- Skriver [14] used the LMTO surface Green's fucntion method. This approach is closely related to our own ASA-LMTO calcualtions, but includes the essential surface dipole contributions.

- Miedema [15] used a semi-empirical approach based on relations between vaporization energy (cohesive enrgy), surface energy and electron density. The numbers cited by him are bascially obtained from liquid drop measurements extrapolated to zero temperature using scaling relations derived in his papers.

- Wawra's [16] approach is also semi-empirical and is based on an assumed proportionaliy between surface energies and elastic constants. Measurements of the elastic cosntants as function of temperature allow him to predict the temperature dependence of the surface energies.

Wawra [16] gives a value of about 1300 mJ/m^2 for the liquid metal at the melting point and 1600 mJ/m^2 for the solid at the melting point.

CONCLUSION: There appears to be agreement on a zero temperature value of $\gamma^s \approx 2 \pm 0.1$ J/m^2, and a value of about 1.5 $\pm$0.2 J/m^2 at the melting point.

3.3.3 Analysis of wetting studies

In the wetting studies of De Vincent et al. [1] a contact angle $\theta = 157°$ was measured. Using

$$\gamma_{gr/Cu} = \gamma_{gr} - \gamma_{Cu} \cos\theta. \tag{1}$$

with $\gamma_{gr/Cu}$ the interface energy and

$$W = \gamma_{Cu} + \gamma_{gr} - \gamma_{gr/Cu}, \tag{2}$$

$$= \gamma_{Cu}(1 + \cos\theta), \tag{3}$$

and the values deduced above for the surface energies of Cu and graphite, we obtain the adhesion energy W to be $\sim$0.2 J/m^2 and the interface energy

$sim 2.0$ J/m^2. Given the uncertainties, we can essentially take the surface energy of graphite and the adhesion to Cu to be zero, which makes the interface energy about equal to the surface energy of Cu which is about 2 J/m^2.

Since the experiment relates to a liquid metal, one should more properly substitute a value of about 1.3 J/m^2 insterad of 2 J/m^2 in the above. In their analysis, De Vincent et al. [1] obtained rather different values mainly because they use a higher value for the surface energy of graphite. A higher value of the surface energy of graphite may be expected if the physical surface in the experiment corresponds to an average over the basal plane and other (higher energy surfaces of graphite) due e.g. to the existence of steps on the surface. Their value (0.8 J/m^2) is based on the work of Mortimer and Nicholas [17] which however, is based on the questionable assumption that the interface energy between a metal and graphite is the same as for the metal with the corresponding carbide. We believe this to be an overestimate of the surface energy of graphite.

This does not, of course affect the validity of DeVincent et al.'s measurements of the contact angles as function of alloy additions. Contact angle measurements on HOPG graphite may be useful to obtain a better estimate of the true contact angle on the basal plane and hence the present estimates of the adhesion energy.

3.3.4 Other studies of metal/graphite interaction

Several studies exist of the interaction between graphite thin films or monolayers and metal surfaces. One context in which these arise is in studies of catalysis. Deposition of carbon containing molecules (CO, CH_x, etc.) on metal surfaces leads to the formation of a graphite monolayer on the surface under suitable heating treatments. Essentially this occurs under conditions of a sufficiently high carbon coverage which allows the carbon atoms to get close enough to each other to form a π-bonded system. In the case of a lower coverage, the carbon atoms prefer to make a stronger bond to the substrate, which leads to a surface phase resembling the bonding in carbides and therefore called carbidic. A good summary of the physics of these surface systems can be found in the theoretical work of Feibelman [18].

Several experimental studies of this also exist, e.g. work by Rosei et al. [19, 20], Papagno et al.[21], McConville et al. [22] on Ni/graphite and Aizawa et al .[23] on TaC/graphite. Several of these authors mention the

existence of a charge transfer between the metal and graphite as evidenced by photoemission and EELS. The work of Aizawa et al. [23] showed that this can lead to a softening of the bonds in the graphite layer as evidenced by phonon softening measured by EELS.

In the case of Ni/graphite the interaction was found strong enough to force a registry of the graphite monolayer with the Ni substrate, as evidenced by SEXAFS [20] measurements.

We also found evidence for a charge transfer between Pt and graphite in the photoemission studies of Eppell [21] at CWRU.

Finally, we mention that graphite metal interactions have been of interest in the context of scanneling tunneling microscopy. Graphite is a very much used substrate in these studies and metal tip to graphite interactions have hence been studied. We mention for example the theoretical work of Tománek and Zong [25] using first-principles density functional calculations of a metal atom interacting with a graphite surface. This work shows that the repulsive interaction is weaker for an atom approaching the surface above the hollow position than for the metal on top of carbon position. The bonding minimum occurs at a distance of ~2.6 Å and is extremely weak. This confirms our qualitative conclusions of weak bonding. A semi-empirical parametrization of the bondign curve obtained from first-principles is given in this work. This may be useful for future simulations of Pd/graphite interaction.

4 Conclusions and Recommendations

Our computational results indicate that the bonding between Cu and graphite is weak because of the "closed shell" nature of graphite and the full d-shell of Cu. We nevertheless found some indication of charge transfer which is worth further study. Also, transition metals with partially filled d-bands may show somewhat stronger interactions with graphite. This is indicated by the work on monolayers of graphite on these metals. The encouraging improvements in wetting found by alloying additions of transition metals (TM) to Cu also point in that direction.

An obvious line of future work would thus be to extend the work to transition metals. In order to obtain accurate quantitative results on the energetics, full-potential calculations are required.

An important question is whether a substantially stronger bonding oc-

curs for these TM metals at abrupt interfaces with graphite, or, whether the improved bodning is due to carbide formation and chemical reaction. The wetting studies point to the existence of an interfacial phase and chemical interactions. It is of great interest scientifically to study the early stages of this process. The transition metal carbides have the rocksalt structure. Viewed along the {111} direction, this structure consists of alternatingly carbon and TM atom layers. The only difference with graphite/TM superlattices of the type we have studied is the number of carbon atoms per TM atom in the carbon layer. Transition metal carbides have very strong bonding resulting in refractory compounds. There must thus be a gradual transition in bonding strength from the metal/graphite interface to the carbidic bond. Essential for the formation of the carbide appears to be that the carbons remain sufficiently far apart so as not to form π-bonds among each other. The question is thus how the metal inserts itself in the first layers of graphtie and breaks up the strong graphitic interlayer bond. Studies on model systems could provide important insights in the way the carbide interfacial layer is formed. Obviously, diffusion and kinetic effects will also be of great importance in this reaction.

Even when we accept the formation of a transition metal carbide, the question remains how the latter bonds to graphite. At an abrupt graphite/TM-carbide interface, the bonding might be similarly weak as for the graphtie/metal interface. The imporved bodning may be due to some interlocking of phases and bonding across non-basal plane surfaces of graphite. This aspect could be studied by Electron-microscopy observations of the interfacial layer.

We also recommend surface science studies of the interaction between graphite and metal by depositing a thin layer of graphite on various transition metals (or vice versa) as a function of temperature. We also recommend doing the contact angle measurements in UHV and on HOPG graphite in order to avoid any extrinsic effects.

Finally, with continued support for our theory project, reliable values for the energetics could be obtained using full-potential calculations. The FP-LMTO method has been proven to provide accuracies comparable to the LAPW method. The latter has proven to provide accurate values for graphite and metal surfaces. Future theoretical research projects related to the present work could include:

- full-potential LMTO calculations of graphite, Cu-surface energies and Cu/graphite interfaces;
- similar studies for a transition metal such as Ti and Cr;
- studies of systems intermediate between Ti/graphite and TiC.

Accomplishment of these research goals however, will require a more substantial effort than was possible withing the framework of this grant.

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FIGURE CAPTIONS

Fig. 1 Band structure of a monolayer of graphite.

Fig. 2 Band structure of AB-stacked hexagonal graphite

Fig. 3 Density of states of a monolayer of graphite

Fig. 4 Local densities of states of Cu {111} surface

Fig. 5 Local densities of states at Cu {111}/graphite {0001} interface

FIG. 1

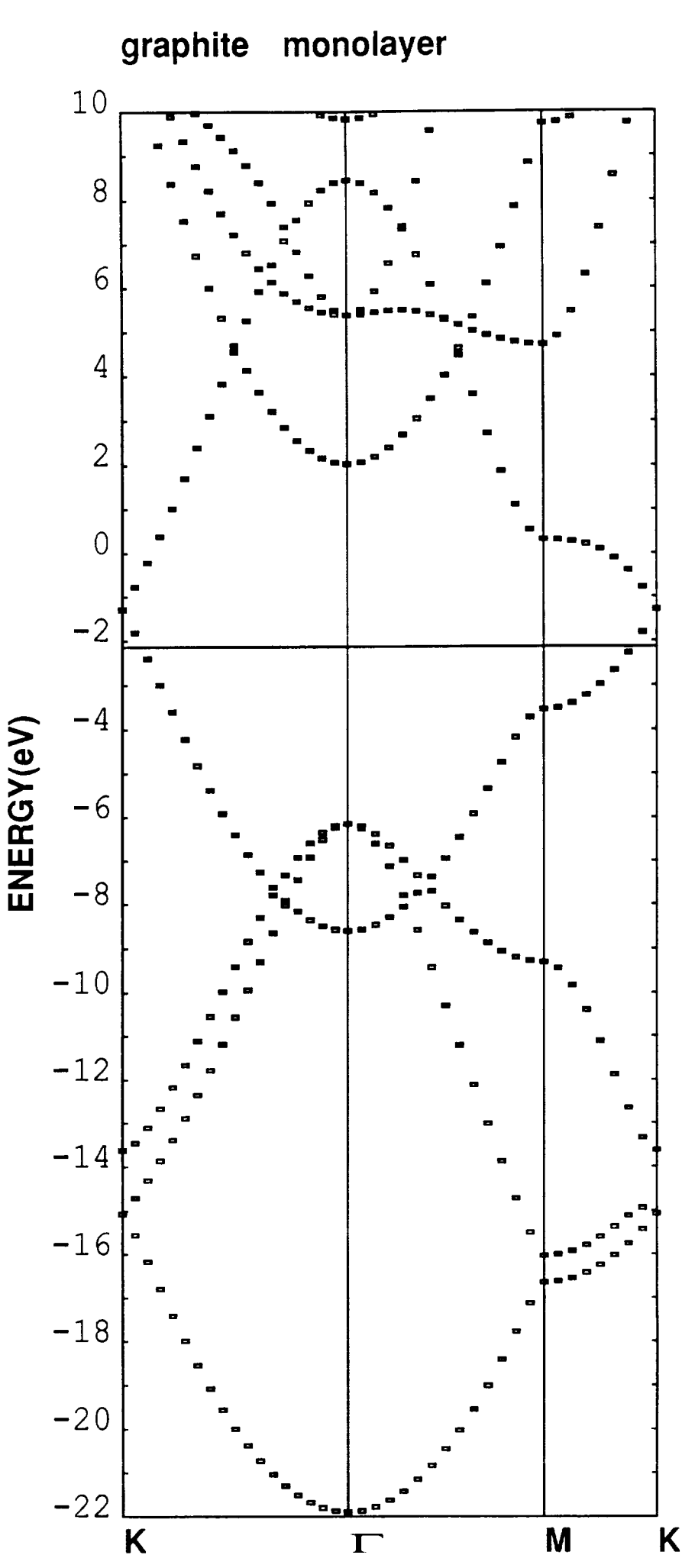

graphite monolayer
ENERGY(eV)
10
8
6
4
2
0
-2
-4
-6
-8
-10
-12
-14
-16
-18
-20
-22
K
Γ
M
K

FIG. 2

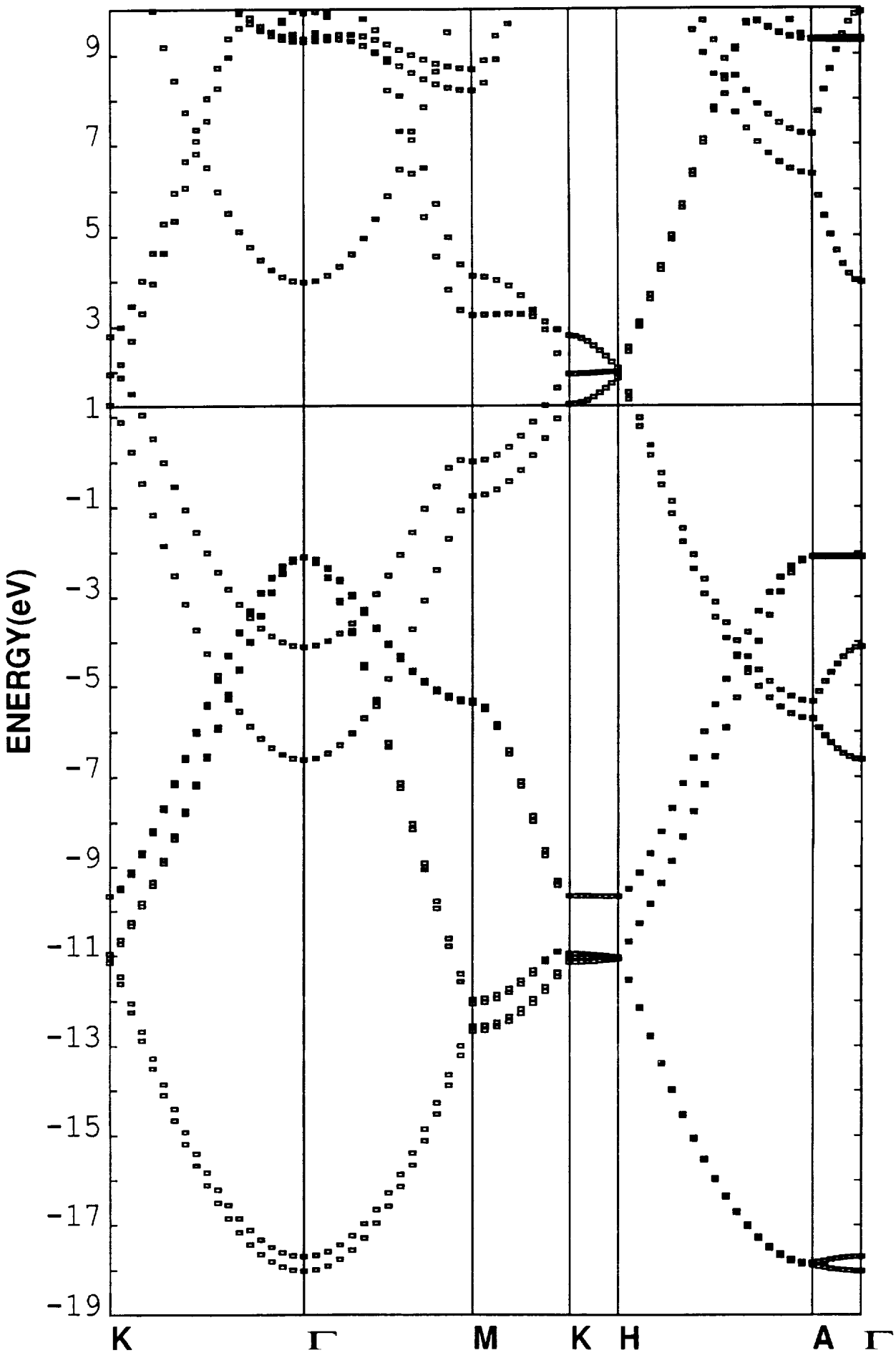

C (graphite) (AB) a=4.6525 c/a=2.7
ENERGY(eV)
9
7
5
3
1
-1
-3
-5
-7
-9
-11
-13
-15
-17
-19
K
Γ
M
K
H
A
Γ

FIG. 3

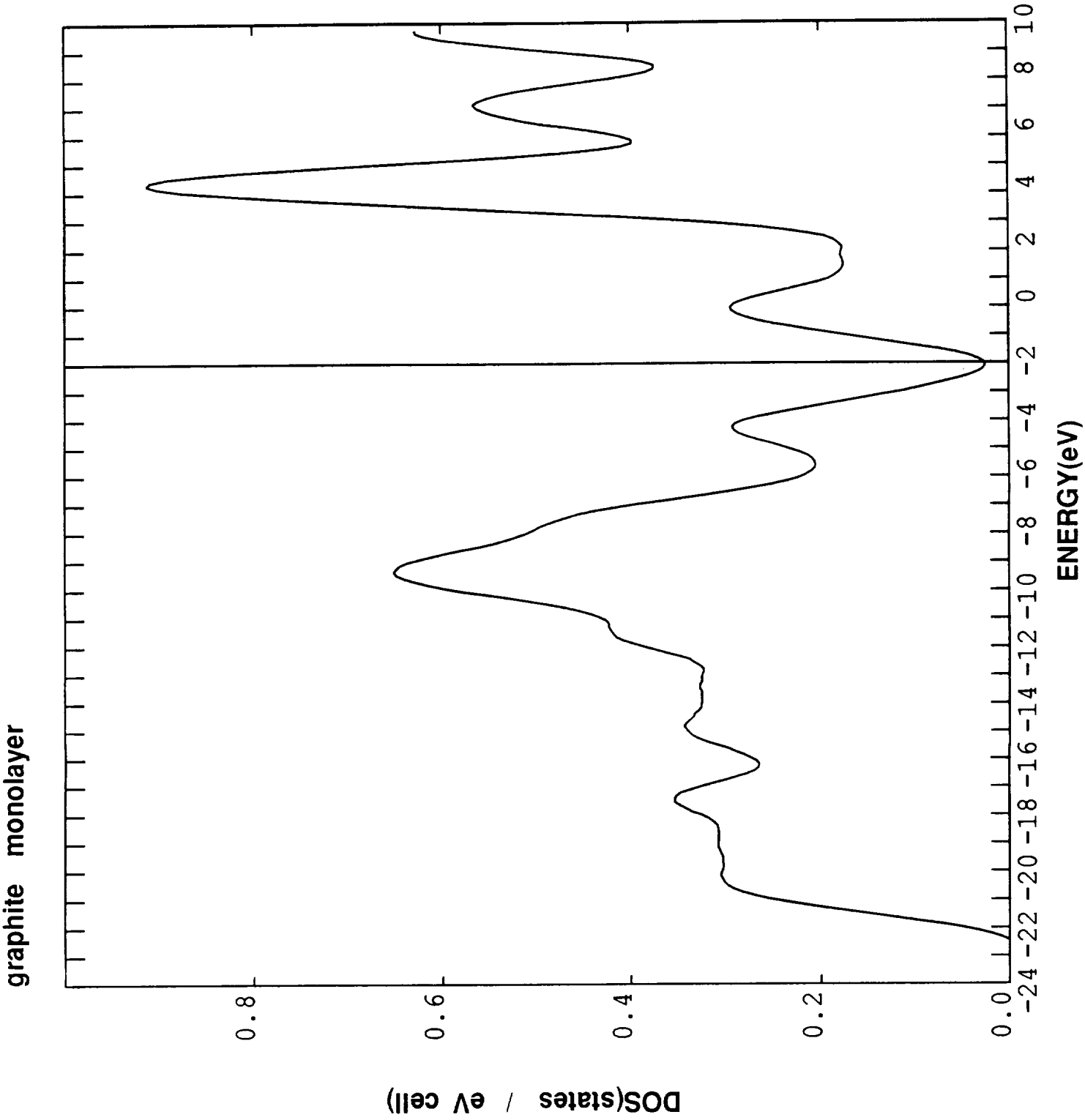

graphite monolayer
DOS(states / eV cell)
0.0
0.2
0.4
0.6
0.8
-24 -22 -20 -18 -16 -14 -12 -10 -8 -6 -4 -2 0 2 4 6 8 10
ENERGY(eV)

FIG. 4

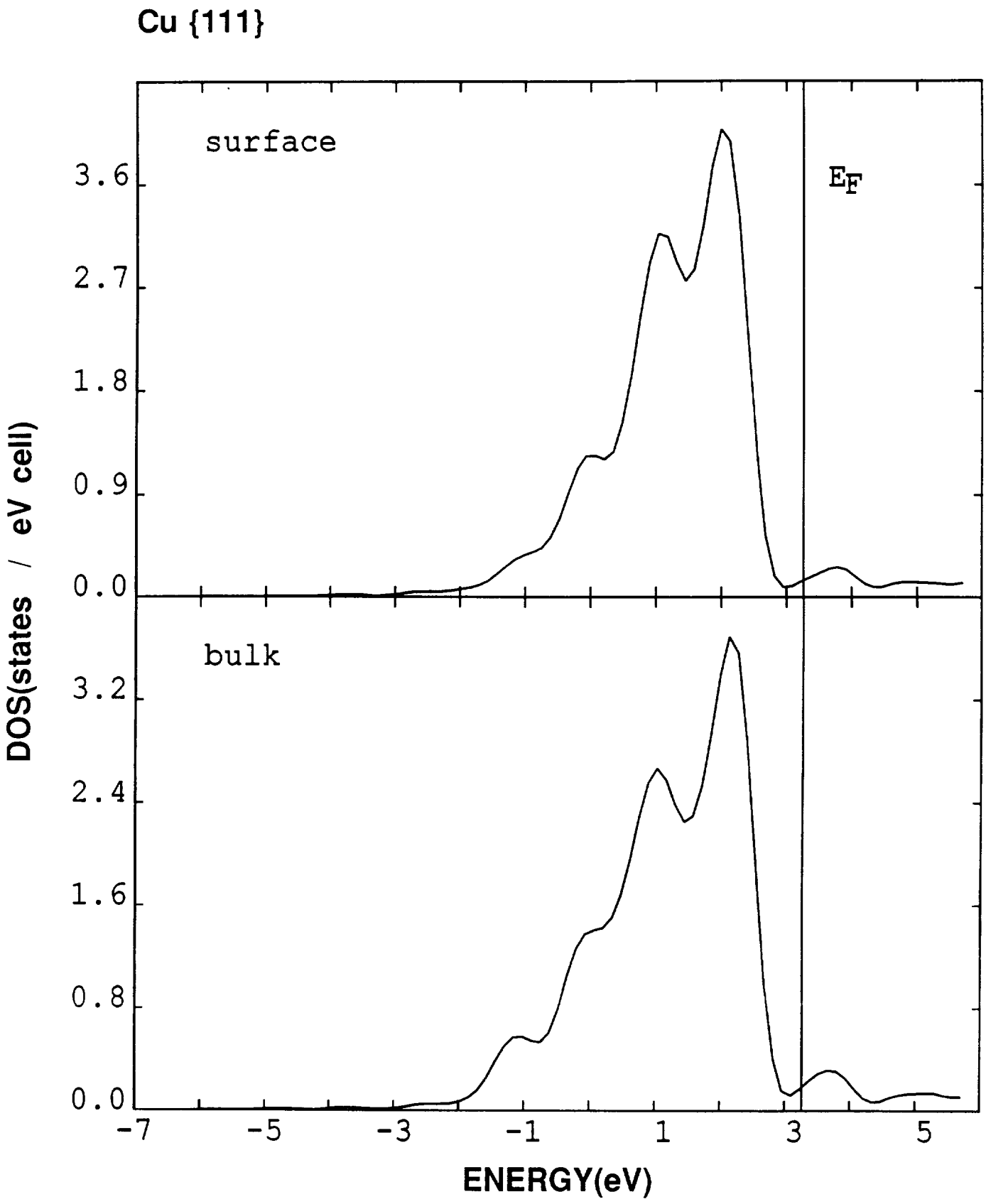
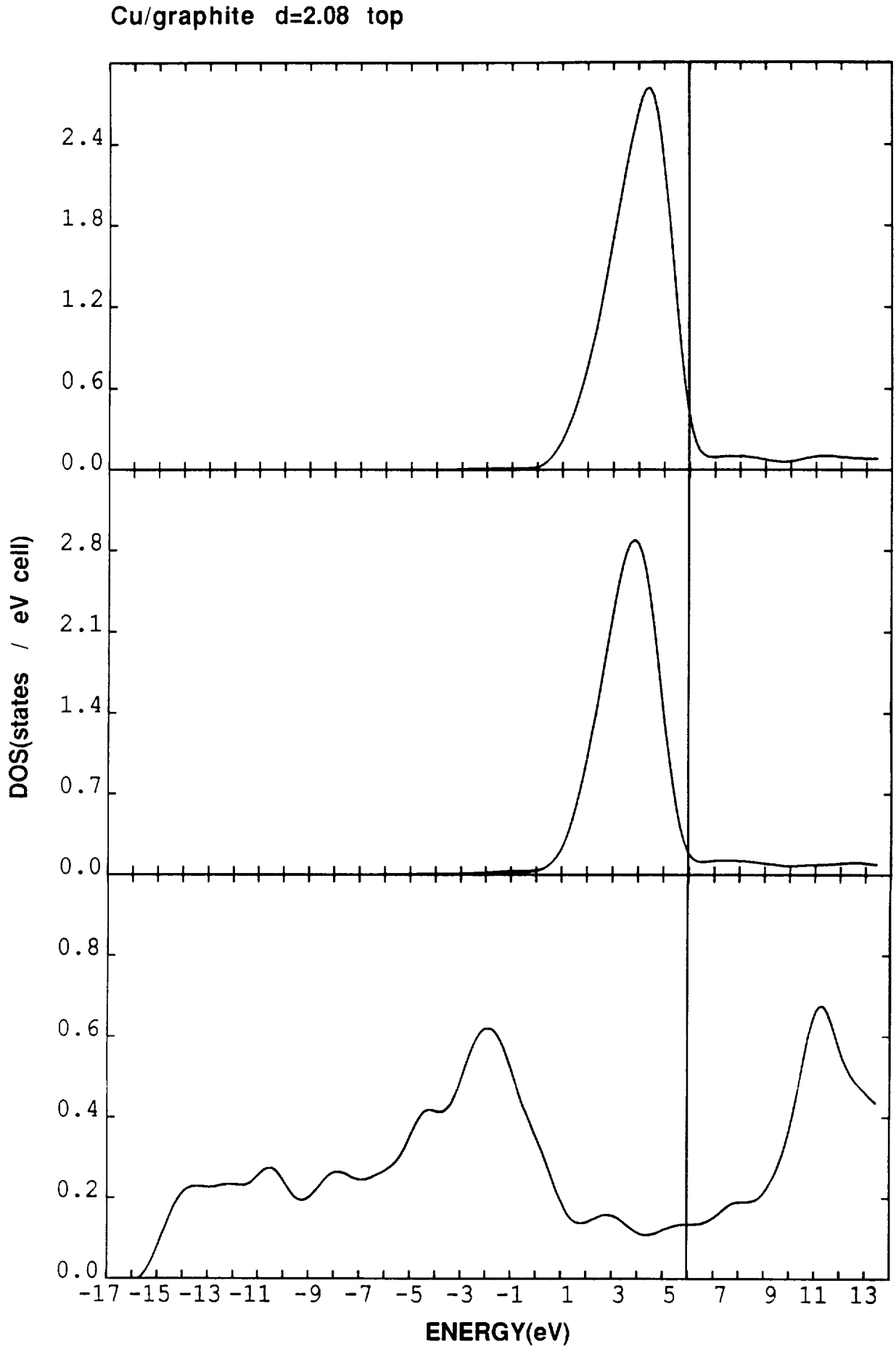

Cu {111}
surface
bulk
E_F
DOS(states / eV cell)
ENERGY(eV)
3.6
2.7
1.8
0.9
0.0
3.2
2.4
1.6
0.8
0.0
-7
-5
-3
-1
1
3
5

FIG. 5


Cu/graphite d=2.08 top
DOS(states / eV cell)
2.4
1.8
1.2
0.6
0.0
2.8
2.1
1.4
0.7
0.0
0.8
0.6
0.4
0.2
0.0
-17 -15 -13 -11 -9 -7 -5 -3 -1 1 3 5 7 9 11 13
ENERGY(eV)